Co(III) complexes. Also, water exchange of $Co(NH_3)_5OH^{2+}$ is slower than that of $Co(NH_3)_5OH_2^{3+}$ and no CO_2 catalysis has been noted,[5] although the carbonate complexes of Co(III) are stable.[1] These results imply that the flip process is less likely for Co(III) than for Cr(III). This may be attributed to the greater tendency of d^3 ions, relative to d^6 ions, to adopt seven-coordinate structures.[9,10]

This also may account for the marked difference between the oxygen exchange behavior of $Cr(C_2O_4)_3^{3-}$ (all 12 oxygens equivalent) and $Co(C_2O_4)_3^{3-}$ (6 oxygens exchange more rapidly, 6 more slowly).[11] Rapid intramolecular oxygen exchange may occur in $Cr(C_2O_4)_3^{3-}$ without one-ended dissociation.[12]

Acknowledgment. We are grateful for support from the U. S. Atomic Energy Commission and the U. S. Air Force Office of Scientific Research. We are also grateful to Brookhaven National Laboratory for use of the Consolidated-Nier mass spectrometer and especially to Dr. Norman Sutin for gracious hospitality to one of us (W. A.). We are also grateful to Dr. Thomas Kallen for checking the results reported in Figure 3.

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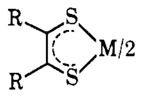
Dithiotropolonates. II.[1] The Synthesis and Properties of Dithiotropolone and Its Metal(II) Complexes

C. E. Forbes[2] and R. H. Holm

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received November 13, 1969

Abstract: Dithiotropolone (**15**) has been prepared in *ca.* 30% yield from tropolone *via* the reaction of hydrosulfide ion with 1,2-diethoxytropylium tetrafluoroborate (**13**) and isolated as deep red, air-sensitive crystals. Infrared, electronic, and mass spectral characterization data are reported. The tropylium species **13** has been shown to be a potentially valuable intermediate in the synthesis of 1,7-disubstituted 1,3,5-cycloheptatrienes. Reactions with primary amines alone and with hydrosulfide yield N,N-disubstituted aminotroponeimines (**16, 17**) and N-substituted aminothiotropones (**18**), respectively, in 40–75% yield. Dithiotropolone or its sodium salt readily reacts with divalent metal salts to afford a series of intensely colored, slightly soluble bis-chelate complexes, M(SST)$_2$ (**7, 8**). Probable ground-state electronic structures of these complexes are discussed in relation to neutral bis(dithiolene) complexes (**1**). Spectral and polarographic studies reveal that, like the dithiolenes, M(SST)$_2$ species (M = Ni, Pd, Pt) exhibit intense near-infrared absorption bands and are reducible in two apparent one-electron processes, which, in contrast to those of the dithiolenes, are irreversible and occur at potentials *ca.* 0.75–1.0 V more negative. Electrochemical activity has also been established for Cu(SST)$_2$, Zn(SST)$_2$, Cd(SST)$_2$, and for Ni and Zn complexes of 2-mercaptotropone, N,N-dimethylaminotroponeimine, and N-methylaminothiotropone; in most cases the redox processes are irreversible. The presently available information does not permit a detailed assessment of the relation between electronic structures of dithiolene and dithiotropolonate complexes, the latter of which are under further investigation.

The chemistry of metal complexes in which all ligating atoms are sulfur has undergone a most significant advance in recent years. Numerous new species containing four-, five-, and six-membered chelate rings have been prepared, but perhaps the most striking developments have occurred as a consequence of the extensive investigations of those complexes possessing unsaturated five-membered rings of general types 1 and 2 (X = Y = S). Such complexes are now generically referred to as dithiolenes[3a] (or dithienes[3b,c]). Bisdithiolenes have three properties of general importance: (i) they undergo redox reactions producing an electron transfer series of at least three members, $[M\text{–}S_4]^{2-} \rightleftharpoons [M\text{–}S_4]^{-} \rightleftharpoons [M\text{–}S_4]^{0}$; (ii) monomeric complexes (with the probable exception of zinc derivatives) are planar irrespective of oxidation level; (iii) metal–ligand bonding is highly covalent and odd electrons in paramagnetic species are extensively delocalized. The last property is responsible for the well recognized ambiguity in assigning formal oxidation states in $[M\text{–}S_4]^z$ species with $z = -1, 0$. While most exhaustively demonstrated for dithiolenes, these properties extend to certain $[M\text{–}(NH)_4]^z$,[4] $[M\text{–}(NH)_2S_2]^z$,[5] and $[M\text{–}O_2S_2]^z$ [6] series of



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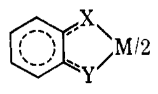

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(2) National Institutes of Health Predoctoral Fellow, 1968–present.

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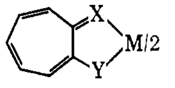
complexes (**2**) which differ significantly from dithiolenes only in the composition of the donor atom set.

In the course of our recent investigations of redox-active bis-chelate complexes derived from unsaturated ligands, we have become interested in the synthesis, structures, and electronic properties—in particular, the redox propensities—of the neutral species **3** formed by chelating, monoprotic 1,7-disubstituted 1,3,5-cycloheptatrienes. Complexes of tropolone ($X = Y = O$) are well known,[7,8] but at least several formed with metal ions of the first transition series appear to be polymerized and thus are unsuitable for our purposes. A few species with $X = S$ and $Y = O$[7] and NR[9] have been prepared but not investigated in any detail. Numerous bis(aminotroponeiminato) complexes ($X = Y = NR$) have been prepared,[10–13] and their structural and electronic properties, especially those of nickel(II) derivatives,[11] examined in some detail.



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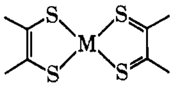
It is generally agreed[3a–c] that the valence-bond representation **4** ⇄ **5** of the neutral bisdithiolenes furnishes the simplest feasible description of ground state electron distribution and the presence of an even-atom ligand system of partial α-dithione character accounts for the marked electron affinity of these species, terminating with the formation of dianions which can be meaningfully formulated in terms of metal(II) and two dithiolate ligands. Similar comments apply to related systems $[M\text{-}X_2Y_2]^z$ with other donor-atom sets. The dithiotropolonates present a potentially interesting contrast to the dithiolenes. The principal contributing VB structures are expected to be **7** and **8**, leading to the delocalized structure **9**, and **10**, which contains two tropylium rings and appreciable negative charge on each of the sulfurs. Dithiolate ⟷ dithione resonance forms *strictly analogous* to **4** and **5** are not accessible to bis(dithiotropolonates) in the ground state. This argument, although very simple,[14] suggests that dithiotropolonates as a class should not exhibit the high degree of electron affinity demonstrated for the dithiolenes, a prediction offered independently during the course of this investigation,[3c] and that other type **3** species as well should not be as easily reduced as their $[M\text{-}X_2Y_2]^0$ counterparts.[3a,4–6]



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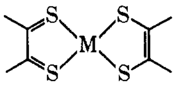

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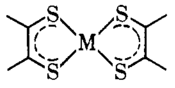

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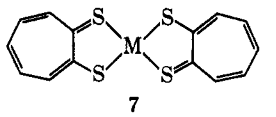

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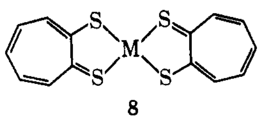

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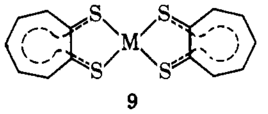

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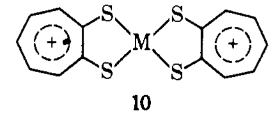

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Neutral complexes of type **3** represent the most extensive group known at the outset of this investigation which contain delocalized five-membered rings, but which lack the specific ground-state electronic features presently considered principally responsible for the strong electron affinities of redox-active $[M\text{-}X_2Y_2]^0$ entities and for the existence of $[M\text{-}X_2Y_2]^z$ electron-transfer series of three[3,5,6] to five[3a,4] members. In order to assess the importance of these features, we have prepared a series of complexes **3** with $X = S$, $Y = O$; $X = S$, $Y = NMe$; $X = Y = NMe$, and $X = Y = S$ and compared their redox and other electronic properties with those of **1** ($R = Me$) and **2**, which have been investigated in considerable detail.

Conspicuously absent from the requisite set of 1,2-disubstituted cycloheptatrienyl ligands already prepared at the beginning of this study was dithiotropolone. The preparation of tropolone[15] has been followed by the synthesis of 2-mercaptotropone[16] and a variety of aminotroponeimines[10,17] and aminothiotropones.[9,17b,18] A reasonably efficient synthesis of dithiotropolone has been devised which is described in this report together with the preparation of a group of bis(dithiotropolonato) complexes and related nickel and zinc species of type **3**. Dithiotropolone has been completely characterized spectroscopically, and the results of an investigation of the spectral and electrochemical properties of the complexes[19] are presented. An earlier report[1] described the synthesis and some of the properties of dithiotropolone and its complexes.

Experimental Section[20]

Preparation of Compounds. Tropolone was obtained from a commercial source (Biddle-Sawyer Corp.) or prepared by the procedure developed by Stevens, *et al.*,[21] in 50% yield. 2-Chlorotropone was obtained from tropolone in 80% yield by reaction with thionyl chloride.[15] 1-Methylimino-7-methylaminocyclohepta-

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[12] W. R. McClellan and R. E. Benson, *ibid.*, **88**, 5165 (1966).

[13] D. R. Eaton, W. R. McClellan, and J. F. Weiher, *Inorg. Chem.*, **7**, 2040 (1968).

[14] It is to be noted that all planar four-coordinate complexes containing five-membered chelate rings which are known to undergo a series of two or more one-electron transfer reactions[3] possess a level of oxidation describable in terms of two equivalent VB structures analogous to **4** and **5**. For an elaboration of the electronic structures of dithiolenes in MO terms, *cf.* ref 3a–c and literature cited therein.

[15] W. E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **74**, 5683 (1952).

[16] T. Nozoe, M. Sato, and K. Matsui, *Proc. Jap. Acad.*, **29**, 22 (1953); *Sci. Rept. Tohoku Univ., First Ser.*, **37**, 211 (1953).

[17] (a) H. Nakao, *Chem. Pharm. Bull.* (Tokyo), **13**, 810 (1965); (b) N. Soma, J. Nakazawa, T. Watanabe, Y. Sato, and G. Sunagawa, *ibid.*, **13**, 819 (1965).

[18] T. Nozoe and K. Matsui, *Bull. Chem. Soc. Jap.*, **34**, 1382 (1961).

[19] The following designations are used for ligand anions: T^T, tropolonate; ST, 2-mercaptotropolonate; NMeST, 2-methylaminothiotroponate; Me_2-ati,[13] N,N′-dimethylaminotroponeiminate.

[20] All melting points were obtained on samples in evacuated capillaries and are uncorrected.

[21] H. C. Stevens, D. A. Reich, D. R. Brandt, K. R. Fountain, and E. J. Gaughan, *J. Amer. Chem. Soc.*, **87**, 5257 (1965).

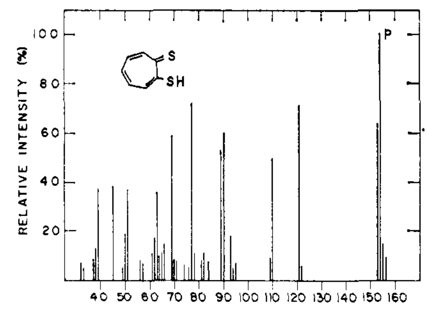

Figure 1. Mass spectrum (70 eV) of dithiotropolone.

triene and 1-methylamino-7-thioxocycloheptatriene were prepared by known methods[9,10] or by the procedures given below. 2-Mercaptotropone was obtained by a published procedure.[16]

1,2-Diethoxytropylium Tetrafluoroborate (13). Freshly prepared triethyloxonium tetrafluoroborate (76 g, 0.40 mol) and a solution of 41 g (0.29 mol) of 2-chlorotropone in 250 ml of dry dichloromethane were stirred for 30 hr under a nitrogen atmosphere at room temperature. After removal of the solvent under reduced pressure, a brown solid was obtained. A very small portion was purified by recrystallization from dry tetrahydrofuran yielding a white solid (mp 80–81° dec.), and was identified by its pmr spectrum as 1-ethoxy-2-chlorotropylium tetrafluoroborate: CD_2Cl_2, τ 8.30 (triplet, 3, CH_3), 5.12 (quartet, 2, CH_2), 1.16 (multiplet, 5, ring H). The brown solid was refluxed with 250 ml of absolute ethanol for 3 hr, and the solvent stripped off under reduced pressure. The resultant brown oily solid was purified by recrystallization from two *ca.* 1500-ml portions of dry tetrahydrofuran, affording 53 g (68%) of the product as white plates: mp 115–116°; pmr ($CDCl_3$): τ 8.18 (triplet, 6, CH_3), 5.17 (quartet, 4, CH_2), 1.33 (multiplet, 5, ring H).

Anal. Calcd for $C_{11}H_{15}O_2BF_4$: C, 49.66; H, 5.68; F, 28.57. Found: C, 49.96; H, 5.99; F, 29.40.

The compound is unstable to moisture and should be manipulated and stored under anhydrous conditions.

Dithiotropolone (2-Mercaptocycloheptatrienethione) (15). All operations were carried out in a dry nitrogen atmosphere. A solution of 5.00 g (18.8 mmol) of 1,2-diethoxytropylium tetrafluoroborate in 150 ml of absolute ethanol was treated with 50 ml of a 0.75 *M* solution of sodium hydrosulfide (37.5 mmol) in absolute ethanol (prepared by dissolving 0.87 g of sodium in the specified volume and saturating the solution with dry hydrogen sulfide). After 15 min of reaction at room temperature the mixture was filtered to remove sodium tetrafluoroborate. The filtrate was taken to dryness *in vacuo* during which process the temperature of the solution was maintained at or below room temperature. The reddish brown solid was washed twice with dichloromethane and dried *in vacuo*. The crude sodium dithiotropolonate (3.0 g) obtained in this way was not further purified. It was dissolved in 250 ml of oxygen-free water, the solution filtered, and the deep red-brown filtrate treated with 10 ml of an oxygen-free 5.5 *M* hydrochloric acid solution. The red-orange precipitate which formed immediately was collected by filtration and vacuum-dried. Purification was effected by slow sublimation at 38° (10^{-3} mm) to afford 1.64 g (57%) of dithiotropolone as deep red crystals; mp 72–73°.

Anal. Calcd for $C_7H_6S_2$: C, 54.51; H, 3.92; S, 41.57. Found: C, 54.51; H, 3.92; S, 41.56.

Dithiotropolone is unstable to oxygen and should be manipulated and stored under a nitrogen atmosphere. Its spectroscopic properties are summarized in Table I. Pmr and mass spectra are shown in Figures 1 and 2.

The following three preparations serve to indicate the presently explored utility of 1,2-diethoxytropylium tetrafluoroborate as a reactive intermediate in the synthesis of chelating 1,7-disubstituted cycloheptatrienes.

1-*p*-Tolylimino-7-*p*-tolylaminocycloheptatriene (16). A solution of 1,2-diethoxytropylium tetrafluoroborate (1.0 g, 3.8 mmol), *p*-toluidine (0.81 g, 7.5 mmol), and sodium ethoxide (0.26 g, 3.8 mmol) in 30 ml of absolute ethanol was refluxed for 24 hr. The solution was cooled to −10° and water added as necessary to effect separation of an orange crystalline solid. The product was recrystallized twice from ethanol-dichloromethane to yield 0.48 g (43%) of **16**, mp 139–140° (lit.[10] yield 62%, mp 143–144°).

1-Methylimino-2-methylaminocycloheptatriene (17). 1,2-Diethoxytropylium tetrafluoroborate (5.0 g, 19 mmol) and 2.1 g (39 mmol) of sodium methoxide in 50 ml of absolute ethanol were added to ~50 ml of methylamine at −10°. The resulting light yellow solution was stirred at room temperature for *ca.* 3 hr, with protection from moisture. The solution was then poured onto 600 g of ice and after some melting the yellow precipitate was collected by filtration. One recrystallization afforded 1.66 g (60%) of yellow crystals, mp 65–66° (lit.[10] yield 75%, mp 66.5–67°).

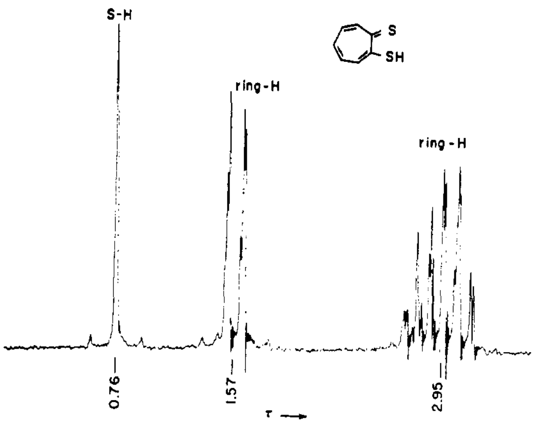

Figure 2. Pmr spectrum (100 MHz) of dithiotropolone in $CDCl_3$ solution.

Table I. Spectroscopic Properties of Dithiotropolone (**15**)

Spectrum	Features
Pmr ($CDCl_3$)	τ 2.95, multiplet, 3, ring-H; τ 1.57, multiplet, 2, ring-H; τ 0.76, 1, SH
Mass spectrum (70 eV)[a]	*m/e* 154 (100, P), 153 (64), 121 (71), 110 (50), 90 (60), 89 (53), 77 (72), 69 (59), 63 (36), 51 (37), 45 (39), 39 (37)
Ir (KBr)	3040 (w), 2445 (m),[c] 1545 (w), 1475 (vs), 1467 (vs), 1425 (vs), 1415 (s), 1385 (m), 1286 (s), 1252 (m), 1231 (s), 1100 (vs), 1087 (sh, m), 1058 (vs), 1017 (w), 996 (w), 988 (vw), 964 (w), 936 (m), 930 (m), 879 (m), 855 (vw), 728 (s), 661 (m), 592 (m), 567 (m), 490 (w), 441 (m)
Uv (cyclohexane)[b]	23,000, 9,560; 29,700 (sh), 4,270; 33,500, 22,100; 43,300, 8,940

[a] Relative intensity (%) in parentheses, only peaks with >20% intensity listed; spectrum obtained using direct inlet method producing somewhat different intensities than reported previously.[1] [b] λ_{max} (cm^{-1}), ϵ (l. $mole^{-1}$ cm^{-1}). [c] 2450 cm^{-1} in Fluorolube mull, shifted to 1725 cm^{-1} upon deuteration.

1-Methylamino-7-thioxocycloheptatriene (18). A solution of 5.0 g (19 mmol) of 1,2-diethoxytropylium tetrafluoroborate in 100 ml of ethanol was added to 25 ml of methylamine at −10°, and the resulting yellow solution stirred at room temperature for 2 hr. Excess sodium hydrosulfide (0.89 g, 16 mmol) in 25 ml of ethanol was then added and hydrogen sulfide bubbled through the solution at a moderate rate for 1 hr. The resultant mixture was poured into 800 ml of ice water. The resultant orange precipitate was collected by filtration and recrystallized from ethanol to afford 1.76 g (62%) of orange crystals, mp 66–67° (lit.[9] yield 88%, mp 67–67.5°).

2,2′-Di-1-thioxocycloheptatrienyldisulfide (19). Dithiotropolone (0.50 g, 3.2 mmol) dissolved in 250 ml of oxygen-free ethanol was treated with an ethanolic solution of iodine (0.49 g, 1.9 mmol). The red solid which separated was collected by filtration and recrystallized from methanol–dichloromethane and then from toluene to give 0.18 g (37%) of the disulfide as violet needles: mp 144–148° with decomposition; pmr (pyridine-d_5): three multiplets centered at *ca.* τ 2.95, 2.23, 1.72; uv ($CHCl_3$) λ_{max} (mμ), ϵ (l. $mole^{-1}$ cm^{-1}): 244, 32,600; 299, 31,100; 428, 19,500.

Table II. Characterization of $M(SST)_2$ and Related Complexes

Complex	Color	Mp, °C[a]	%, calcd C	%, calcd H	%, calcd S	%, found C	%, found H	%, found S
$Ni(SST)_2$[b]	Black	>360	46.05	2.76	35.12	46.23	2.79	35.25
$Pd(SST)_2$[b]	Violet	>360	40.72	2.44	31.07	41.42	2.65	31.30
$Pt(SST)_2$[b]	Black	>360	33.53	2.01	25.57	34.00	2.23	25.61
$Cu(SST)_2$[c]	Green-black	268 dec	45.44	2.72	34.66	45.39	2.85	34.58
$Zn(SST)_2$[d]	Red	306 dec	45.22	2.71	34.49	45.20	2.78	34.15
$Cd(SST)_2$[d]	Red-brown	240 dec	40.14	2.41	30.61	40.04	2.79	30.04
$Ni(SNMeT)_2$[e,f]	Violet	233–234	53.51	4.49	17.85	53.77	4.68	17.91
$Zn(ST)_2$[e]	Yellow	214–215	49.50	2.79	18.87	49.78	2.84	18.78
$Zn(SNMeT)_2$[e,g]	Orange	257–258.5	52.53	4.41	17.53	52.94	3.89	17.80
$Zn(Me_2\text{-}ati)_2$[h]	Yellow	192.5–193	60.09	6.16		60.37	6.27	

[a] Uncorrected, obtained *in vacuo*. [b] Recrystallized from pyridine. [c] Recrystallized from toluene. [d] Recrystallized from xylene. [e] Recrystallized from dichloromethane–methanol. [f] % N calcd, 7.80; found, 7.65. [g] % N calcd, 7.66; found 7.85. [h] % N calcd, 15.58; found, 15.55.

Anal. Calcd for $C_{14}H_{10}S_4$: C, 54.86; H, 3.29; S, 41.84. Found: C, 54.94; H, 3.39; S, 41.68.

Bis(dithiotropolonato)metal(II) Complexes, $M(SST)_2$ (7,8). These were obtained by reaction of crude sodium dithiotropolonate and a metal salt or dithiotropolone and a metal acetate in 2:1 mole ratio in aqueous and ethanol solutions, respectively. Li_2PdCl_4 and K_2PtCl_4 were employed in the preparation of the palladium(II) and platinum(II) complexes. The precipitate which formed immediately in all cases was digested on the steam bath for 1 hr to increase particle size, filtered, and dried *in vacuo*. The complexes were purified by two recrystallizations from an appropriate solvent and then heated at 100° *in vacuo* for at least 4 hr. Characterization data and solvents used for recrystallization are given in Table II.

Other Complexes. Bis(1-methylaminato-7-thioxocycloheptatriene)nickel(II) and -zinc(II) and bis(2-mercaptotropolonato)zinc(II) were prepared by addition of an aqueous solution of the metal acetate (1 equiv) to 2 equiv of the ligand in methanol. The complexes were recrystallized from dichloromethane–methanol and then heated at 100° *in vacuo* for at least 4 hr. Bis(N,N-dimethylaminotroponeiminato)zinc(II) was obtained by a nonaqueous chelation procedure described earlier.[12] It was purified by two recrystallizations from *n*-heptane and one from methanol and isolated in the pure condition in 40% yield. Characterization data are listed in Table II.

Physical Measurements. Proton resonance spectra were obtained using a Varian HR-100 or T-60 spectrometer. Mass spectra were determined using a Hitachi Perkin-Elmer RMU-6D spectrometer operating at 70 eV. Electronic spectra were recorded on a Cary Model 14 spectrometer and infrared spectra on a Perkin-Elmer Model 337 grating instrument. An ORNL model 1988 polarograph equipped with a three-electrode configuration and modified for cyclic voltammetry was employed for electrochemical measurements. Solutions were prepared using purified DMF as solvent and were $\sim 10^{-3}$ *M* in complex and 0.05 *M* in tetra-*n*-propylammonium perchlorate as the supporting electrolyte. A rotating platinum or dropping mercury electrode was used as the working electrode, and potentials were measured at 25° *vs.* a saturated calomel reference electrode.

Results and Discussion

Synthesis and Characterization of Dithiotropolone. Unpublished work by other investigators performed prior to the inception of this study had revealed that reaction of tropolone (**11**) with P_4S_{10} alone or in the presence of metal ions yielded as the only identifiable product small amounts of 2-mercaptotropone.[22] Additionally, reaction of tropolone with hydrogen sulfide and hydrochloric acid in the presence of metal salts failed to yield dithiotropolonate complexes;[23] bis(dithio-β-diketonato) complexes have been successfully prepared from the parent β-diketone under similar conditions.[24] With these results at hand, it was concluded that a reaction sequence involving direct substitution of hydrosulfide groups on the C_7 ring was required. The synthesis was based on the formal electronic equivalence of –O– and –CH=CH– in unsaturated ring systems, with the consequence that, for example, 4H-pyran-4-one and 4H-pyran-4-thione can be considered as heterocyclic tropone analogs and pyrylium salts as heterocyclic tropylium analogs.[25] The observations that 2,6-dimethyl-4H-pyran-4-one[26] and 4H-thiopyran-4-one[27] are readily alkylated to form pyrylium salts, which in turn are converted to the corresponding pyran-4-thione by treatment with hydrosulfide,[28] prompted a further examination of this analogy.

The reported ethylation of tropone to the ethoxytropylium ion[29] suggested a related reaction involving the formation of a 1,2-disubstituted tropylium species which would be subject to sequential nucleophilic attack by hydrosulfide yielding the desired product. Accordingly, tropolone was converted to 2-chlorotropone[15] (**12**), which when treated with triethyloxonium tetrafluoroborate in dichloromethane afforded 1-ethoxy-2-chlorotropylium tetrafluoroborate, identified by its pmr spectrum. This material in refluxing ethanol readily produced 1,2-diethoxytropylium tetrafluoroborate (**13**) in 68% yield from **12**. Reaction of **13** with 2 equiv of sodium hydrosulfide in absolute ethanol resulted in smooth conversion to sodium dithiotropolonate (**14**). Acidification of **14** with aqueous hydrochloric acid produced dithiotropolone (**15**), which was obtained in 57% yield from **13** after purification by sublimation. This reaction scheme results in a 39% yield of pure product based on 2-chlorotropone, or an *ca.* 30% overall conversion from tropolone.

Spectral characterization data for dithiotropolone are set out in Table I. The mass spectrum, shown in Figure 1, reveals an abundant parent ion peak at *m/e* 154. Prominent peaks at decreasing *m/e* values indicate expulsion of H, SH, CS, S_2, and S_2H producing the species $C_7H_5S_2^+$, $C_7H_5S^+$, $C_6H_6S^+$, $C_7H_6^+$, and $C_7H_5^+$, respectively. The feature at *m/e* 77 is assigned to $C_6H_5^+$. The spectrum of monodeuteriodithiotropolone, prepared from the sodium salt in acidic D_2O solution, is, where applicable, consistent with the formation of such

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(22) J. P. Fackler and E. L. Muetterties, private communications.

(23) R. L. Martin, private communication.

(24) (a) C. G. Barraclough, R. L. Martin, and I. M. Stewart, *Austr. J. Chem.*, **22**, 891 (1969); (b) A. Ouchi, M. Nakatani, and Y. Takahashi, *Bull. Chem. Soc. Jap.*, **41**, 2044 (1968).

(25) M. Ohta and H. Kato, *ibid.*, **32**, 707 (1959).

(26) H. Kato, T. Ogawa, and M. Ohta, *ibid.*, **33**, 1467 (1960).

(27) G. Traverso, *Chem. Ber.*, **91**, 1224 (1958).

(28) For other examples *cf.* R. Mayer, W. Broy, and R. Zahradník, *Advan. Heterocyclic Chem.*, **8**, 219 (1967).

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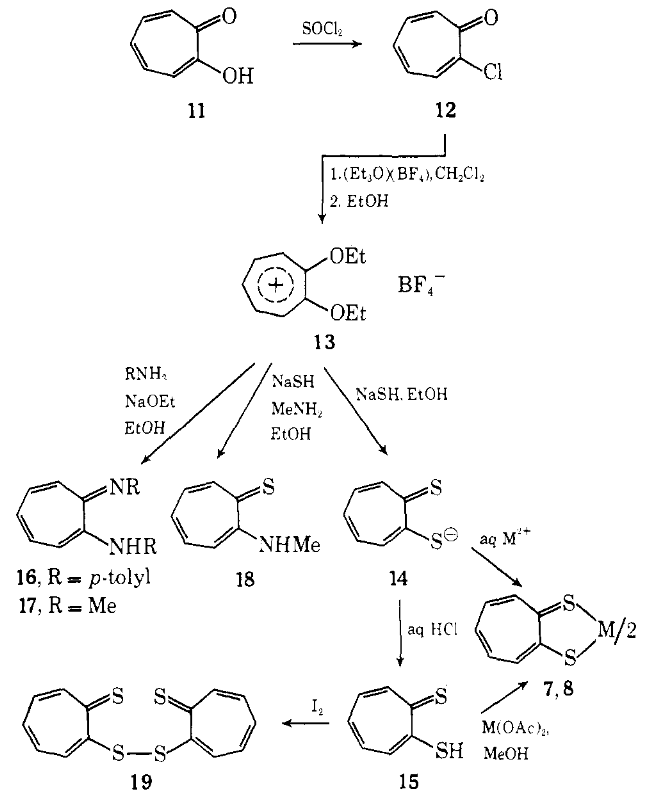
species. The loss of CS is presumably analogous to the loss of CO which is the primary fragmentation step in the 70-eV spectra of tropolone and 2-mercaptotropone.[30] The latter also exhibits a relatively intense peak arising from loss of CS. The relatively weak peaks at *m/e* 66 and 65 may correspond to the expulsion of CS and CHS fragments from $C_6H_6S^+$, which would parallel the loss of CO and CHO from $C_6H_6O^+$ in the fragmentation pattern of tropolone.[30] The most distinctive feature of the pmr spectrum (Figure 2) is the markedly deshielded resonance position of the S–H proton (τ 0.76), indicating the presence of a hydrogen-bonded chelate ring. Tropolone and 2-mercaptotropone in deuteriochloroform solution also exhibit low field resonances at τ 0.49 and 0.05, respectively. The ring proton signals occur as two well-separated multiplets of intensity ratio 2:3 and have not been definitely assigned. This portion of the spectrum is not clearly related to the complex ring proton features of 2-mercaptotropone and N,N′-dimethylaminotroponeimine,[10] or of tropolone, for which a complete assignment has recently been presented.[31] The infrared spectrum in the 1400–400-cm^{-1} region is quite similar to that of the disulfide **19** but is not clearly related to those of tropolone, 2-mercaptotropone, or N,N-dimethylaminotroponeimine. The feature at 2450 cm^{-1} (mull) was identified as the S–H stretch by examination of the monodeuterio species, in which this absorption appears at 1725 cm^{-1}.



Reactions of the 1,2-Diethoxytropylium Ion. The successful preparation of dithiotropolonate anion by reaction of hydrosulfide with **13** suggests that the latter, like tropylium ion,[32] might react with a variety of nucleophiles, and thereby function as a valuable precursor to 1,2-disubstituted tropylium ions or 1,7-disubstituted 1,3,5-cycloheptatrienes. Reaction of **13** with 2 equiv of *p*-toluidine or excess methylamine in ethanol in the presence of 1 equiv of base has been found to afford the previously prepared[10] aminotroponeimines **16** and **17** in 40–60% yield. Similarly, the treatment of **13** with excess methylamine and 1 equiv of hydrosulfide in ethanol gives the known[9] aminothiotropone in 60% yield. These reactions, while producing somewhat lower yields than those employed in the original syntheses of aminotroponeimines[10] and aminothiotropones,[9] have the distinct advantage of not requiring the difficultly accessible 5,5,6,6-tetrafluoro-1,3-cycloheptadiene used in those syntheses. Further, **13**, being readily prepared in *ca.* 70% yield from 2-chlorotropone, is as readily obtainable a starting material as are cycloheptimidazol-2(1H)-one, 2-methoxytroponeimine, and 2-aminotropones, which have been utilized in more recent syntheses of aminotroponeimines[17] and aminothiotropones.[17b,18] Reaction of **13** with other nucleophiles is currently under study.

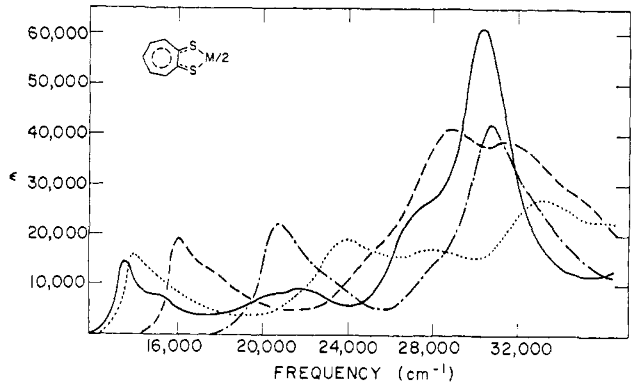


Figure 3. Electronic spectra of bis(dithiotropolonato)metal(II) complexes in DMF solution: ——, Ni(SST)$_2$; – – –, Pd(SST)$_2$; ·····, Pt(SST)$_2$; —·—, Zn(SST)$_2$.

Properties of M(SST)$_2$ Complexes. Six bis(dithiotropolonato)metal(II) complexes have been prepared and characterized. As a class these complexes are intensely colored in the solid state and in solution, very slightly soluble in noncoordinating solvents, and somewhat more soluble in coordinating solvents such as pyridine and DMF. Their solubility in the latter solvents (*ca.* 10^{-3} *M*) is, however, too low to permit molecular weight measurements. Infrared, electronic spectral, and polarographic data are set out in Tables III, IV, and V; electronic spectra of four of the complexes are given in Figure 3. The composition of the complexes has been additionally confirmed by mass spectroscopy. The 70-eV spectra of the representative Ni and Zn species exhibit parent ion peaks ($C_{14}H_{10}S_4M^+$) and others assignable to $C_7H_5S_2M^+$, $C_7H_5S_2^+$, $C_7H_5S^+$, $C_7H_5^+$, and $C_6H_5^+$.

All complexes except Cu(SST)$_2$ are diamagnetic as expected. An X-ray study of Ni(SST)$_2$ currently underway has established a planar structure,[33] consistent with the diamagnetism of this complex. The isotropic epr

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(32) D. Lloyd, "Carbocyclic Non-Benzenoid Aromatic Compounds," Elsevier Publishing Co., Amsterdam, 1966, Chapter VI.

(33) R. Eisenberg, private communication.

Table III. Representative Infrared Data for M(SST)$_2$ Complexes in KBr

Complex	ν, cm^{-1}
Ni(SST)$_2$	3035 (vw), 3015 (w), 3005 (vw), 1570 (m), 1560 (m), 1480 (m), 1460 (w), 1442 (w), 1415 (s), 1405 (s), 1269 (s), 1254 (m), 1234 (m), 1179 (w), 1086 (s), 1081 (m), 1064 (s), 1049 (sh, m), 1000 (w), 979 (vw), 975 (vw), 940 (m), 923 (vw), 907 (w), 885 (m), 842 (vw), 719 (s), 589 (m), 569 (m), 495 (w)
Cu(SST)$_2$	3030 (vw), 3015 (vw), 1570 (m), 1485 (m), 1475 (m), 1460 (w), 1445 (m), 1420 (s), 1390 (s), 1278 (s), 1252 (m), 1237 (s), 1184 (w), 1084 (s), 1079 (m), 1060 (vs), 1046 (w), 1007 (w), 979 (w), 941 (m), 909 (w), 884 (m), 845 (vw), 749 (w), 720 (s), 692 (vw), 595 (m), 565 (m), 495 (w)
Zn(SST)$_2$	3040 (vw), 3020 (vw), 1575 (m), 1470 (s), 1455 (s), 1440 (w), 1420 (s), 1410 (s), 1390 (s), 1284 (s), 1264 (m), 1248 (m), 1238 (s), 1188 (w), 1077 (s), 1058 (vs), 1042 (w), 1010 (w), 994 (w), 974 (m), 947 (s), 940 (m), 915 (w), 883 (m), 842 (vw), 722 (vs), 668 (w), 591 (s), 556 (s), 495 (w), 408 (m)

Table IV. Electronic Spectral Data for M(C$_7$H$_5$XY)$_2$ Complexes in DMF Solution

Complex	$\lambda_{\max}$ (ϵ^a)
Ni(SST)$_2$	13,500 (14,600); 15,200 (sh) (7,300); 20,200 (sh) (8,000); 21,600 (9,200); 27,600 (sh) (25,800); 30,500 (61,700)
Pd(SST)$_2$	16,100 (19,500); 17,300 (sh) (13,400); 25,700 (sh) (18,900); 28,800 (41,300); 31,600 (sh) (37,900); 35,000 (sh) (27,900)
Pt(SST)$_2$	14,000 (16,100); 15,200 (sh) (10,900); 22,500 (sh) (12,200); 24,000 (19,100); 27,900 (17,100); 33,200 (26,800); 36,600 (sh) (22,200)
Cu(SST)$_2$	13,400 (736); 19,600 (sh) (18,100); 21,100 (19,200); 22,600 (sh) (17,100); 27,500 (sh) (21,700); 30,700 (35,500)
Zn(SST)$_2$	20,700 (22,100); 23,100 (sh) (12,200); 28,500 (sh) (16,200); 30,700 (41,900)
Cd(SST)$_2$	20,800 (22,900); 21,800 (sh) (19,300); 27,900 (sh) (13,900); 31,000 (41,700)
Ni(ST)$_2$	17,400 (10,400); 18,800 (sh) (9,490); 23,600 (8,950); 29,200 (sh) (11,600); 30,900 (14,100); 35,300 (31,300)
Ni(SNMeT)$_2$	17,800 (sh) (8,260); 19,100 (9,040); 20,500 (sh) (8,540); 25,400 (sh) (13,500); 31,700 (33,100); 36,200 (26,400)
Ni(Me$_2$-ati)$_2$	12,700 (582); 19,600 (sh) (13,200); 21,100 (16,700); 22,100 (sh) (15,900); 27,200 (19,300); 31,200 (20,600); 35,800 (32,300)

[a] Apparent values, uncorrected for underlying absorption.

parameters for Cu(SST)$_2$, $\langle g \rangle = 2.042$, $\langle a \rangle^{63} = 77 \times 10^{-4}$ cm^{-1}, and $\langle a \rangle^{65} = 83 \times 10^{-4}$ cm^{-1} in 60:40 toluene:chloroform (v/v), are typical for spin-doublet copper complexes with a [Cu-S$_4$] core.[3a] The isotropic and anisotropic epr spectra of a series of copper complexes of type **3** with different donor sets X$_2$Y$_2$ have been measured and analyzed and the results will be presented in a forthcoming report.

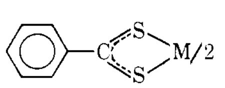
Table V. Polarographic Data for M(C$_7$H$_5$XY)$_2$ Complexes in DMF Solution

Complex	$E_{1/2}$,^{a} V	i_d/C, μA/mM
Ni(SST)$_2$	-1.34, -0.91	12, 15
Ni(ST)$_2$	-1.58,^{b} -1.14,^{b} $+0.72$	17, 18, -22
Ni(SNMeT)$_2$	-2.06,^{b} -1.85, -1.42,^{b} $+0.62$	16, 16, 19, -32
Ni(Me$_2$-ati)$_2$	-1.65,^{b} $+0.24^b$	22, -18
Pd(SST)$_2$	-1.25, -0.89	14, 17
Pt(SST)$_2$	-1.26, -0.85	12, 16
Cu(SST)$_2$	-1.54, -0.39,^{b} $+0.50^b$	15, 17, -15
Zn(SST)$_2$	-1.21, -0.89	11, 16
Zn(ST)$_2$	-1.47,^{b} -1.28	14, 14
Zn(SNMeT)$_2$	-1.75,^{b} -1.53,^{b} $+1.06$	18, 19, -20
Zn(Me$_2$-ati)$_2$	-2.16	19
Cd(SST)$_2$	-1.16, -0.90	8, 15
NiS$_4$C$_4$Me$_4$	-1.08,^{b} -0.09^b	19, 20
Ni(tdt)$_2$	-0.61,^{b} $+0.43$	18, -19

[a] Measured *vs.* sce using a rpe; all waves irreversible unless otherwise indicated; the potentials given here supercede those quoted earlier[1] for certain M(SST)$_2$ which are *ca.* 0.2–0.3 V more positive due to a measurement error. [b] Reversible by cyclic voltammetry.

The electronic spectra of the Ni, Pd, and Pt complexes are dominated by a series of intense absorption bands in the 13,000–36,000-cm^{-1} region. No d–d transitions could be located. The features in the near-infrared region bear a certain resemblance to those observed for neutral dithiolene complexes of these metals (*vide infra*). The 13,400-cm^{-1} band in Cu(SST)$_2$ is probably due to the first spin-allowed d–d band of Cu(II), but its relatively high intensity indicates considerable metal–ligand covalency. The infrared spectra of all M(SST)$_2$ complexes are very similar, exhibiting only minor differences in band positions and relative intensities between the planar Ni, Pd, Pt, and Cu and the presumably tetrahedral Zn and Cd complexes. Measurements were restricted to above 400 cm^{-1}, in which region bands displaying a clear metal sensitivity of frequency were not apparent. Metal-sensitive vibrations in bisdithiolenes which contain some contribution from M–S bond stretching are frequently observed below ~400 cm^{-1}.[34]

The electronic, infrared, and mass spectral data summarized above and in Tables III and IV serve to differentiate unambiguously the present group of complexes from the bis(dithiobenzoato)metal(II) complexes **20**, M(dtb)$_2$, which are analytically indistinguishable from M(SST)$_2$ species. Metal(II) dithiobenzoates have recently been characterized in some detail[35] and Ni(dtb)$_2$[35d] and Pd(dtb)$_2$[35c] shown to be essentially planar and weakly associated in the solid state. For example, Ni(SST)$_2$ and Ni(dtb)$_2$ possess markedly different infrared, electronic, and mass spectra. The latter shows only a weak parent ion peak in its mass spectrum and a fragmentation pattern quite different from that of Ni(SST)$_2$. Ni(dtb)$_2$ exhibits a feature at 13,200 cm^{-1} (ϵ ~980) in its electronic spectrum which has been assigned as a d–d transition.[35b] No related feature is observable in the spectrum of Ni(SST)$_2$ and in addition



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decided spectral differences are observed between the Ni, Pd, and Pt complexes of the SST and dtb[35b] series in the 15,000–35,000-cm^{-1} region.

Comparison with Dithiolene Complexes. As discussed at the outset, one of the motivating factors in this work is the establishment of any significant similarities or differences in the electronic structures of dithiotropolonates and dithiolenes. In this connection the principal point at issue is the relation between a particular $M(SST)_2$ species and a bis(dithiolene) complex of the same metal with the same overall charge. According to earlier considerations as embodied in structures **7**–**10** an $M(SST)_2$ complex of, *e.g.*, Ni, Pd, or Pt, is a "classical" metal(II) species and, therefore, should not possess the electronic properties unique to dithiolenes when compared to other classes of sulfur-bonded metal chelates. Here we present only a brief comparison of $M(SST)_2$ complexes with neutral Ni, Pd, and Pt dithiolenes of type **1** at parity of metal and charge; the most appropriate dithiolenes for this purpose are those with R = H,[36,37] alkyl,[38] and Ph.[38]

Neutral Ni, Pd, and Pt bisdithiolenes possess, in addition to their diamagnetism and planar structures,[39] two conspicuous electronic properties, both of which are associated with their highly delocalized metal–ligand bonding. One is the consistent appearance in the near-infrared region (*ca.* 11,000–14,000 cm^{-1}) of an intense absorption band (ϵ ~20,000–40,000) which has been reasonably assigned as a π–π^* transition[3a–c,36] involving MO's appreciably sulfur and metal in character. Such bands are not observed in the dianionic species or in neutral di-S-alkylated complexes,[40] both of which are reasonably formulated as classical metal(II) complexes. Ostensibly similar features are found in the 13,000–16,000-cm^{-1} region of the $M(SST)_2$ spectra with intensities roughly half as large (*cf.* Figure 3 and Table IV). Band maxima do not follow the same energy order, this being Pt > Ni > Pd for $MS_4C_4Ph_4$ complexes in chloroform[36] and Pd > Pt > Ni for the dithiotropolonates in DMF. The second property of these dithiolenes, which is more significant in the present comparison, is their well documented electrochemical reducibility[3a,b,41] in two generally reversible one-electron steps to afford mono- and dianions. The polarographic data for $M(SST)_2$ complexes in DMF solution are given in Table V. The Ni, Pd, and Pt dithiotropolonates are reducible in two processes, whose diffusion currents indicate an apparent one-electron transfer as judged by comparison with the calibrants $NiS_4C_4Me_4$ and $Ni(tdt)_2$. However, in no case were these processes reversible when investigated by cyclic voltammetry. As a consequence the significance of the half-wave potentials is less clear-cut than for the dithiolenes, which reduce at potentials *ca.* 0.75–1.0 V more positive in DMF.[41] Despite the irreversibility of the $M(SST)_2$ reductions, their far more negative first reduction potentials certainly indicate that they *do not possess the high electron affinities of the dithiolenes.* The polarographic behavior of the Zn, Cd, and Cu dithiotropolonate complexes was also investigated. The first two undergo two irreversible reductions with the second wave of $Cd(SST)_2$ possessing a diffusion current far too low for a one-electron reduction. $Cu(SST)_2$, on the other hand, exhibits a reversible oxidation and first reduction step followed by an irreversible second reduction with all three processes involving a one-electron transfer.

In view of the spectral and electrochemical behavior of $M(SST)_2$ complexes, a series of Ni and Zn complexes of type **3** with X = Y = NMe; X = S, Y = O; and X = S, Y = NMe was prepared and examined. $Ni(ST)_2$[7] and $Ni(Me_2\text{-ati})_2$[10,11] were reported earlier. All of these complexes are electrochemically active, each being reducible in at least one single-electron step and several showing a one-electron oxidation. The majority of these processes again are irreversible by cyclic voltammetry. The Ni complexes do not exhibit the intense near-infrared absorption observed for $Ni(SST)_2$, permitting in the case of $Ni(Me_2\text{-ati})_2$ observation of the first d–d band of the planar isomer[11] at 12,700 cm^{-1}.

The preceding brief description of electronic properties is given at this time only to indicate that neutral Ni, Pd, and Pt dithiolene and dithiotropolonates possess the common properties of two-step electrochemical reducibility and intense near-infrared electronic absorptions. The properties need not necessarily derive from equivalent or analogous electronic structures, but their occurrence in the $M(SST)_2$ series has resulted in our current studies of the redox products of these complexes as well as those of type **3**. A more detailed report on the electronic properties of $M(SST)_2$ and other $M(C_7H_5XY)_2$ complexes will be forthcoming upon completion of synthetic, epr, and electronic spectral investigations and MO calculations of the various ligands and certain of their complexes.

Acknowledgment. This research was supported by the National Science Foundation under Grant GP-7576X and by the Petroleum Research Fund.

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